Updated: 28 January 2020

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CEE 680: Water Chemistry

Lecture #4

Isotopes (cont); Kinetics and Thermodynamics:
Fundamentals of water and Ionic Strength

(Stumm & Morgan, pp.1-15
Brezonik & Arnold, pg 10-18)

(Benjamin, 1.2, 1.3, 1.5)

Best source for stable isotopes is:
Eby, Chapter 6, especially pg. 181-186

Stable Water Isotopes

Type	MW	% of total	ppb
$^{1}H^{1}H^{16}O$	18	99.731	997,310,000
$^{1}H^{1}H^{18}O$	20	0.2000	2,000,000
$^{1}H^{1}H^{17}O$	19	0.03789	378,900
$^{1}H^{2}H^{16}O$	19	0.03146	314,600
$^{1}H^{2}H^{18}O$	21	$6.116x10^{-5}$	612
$^{1}H^{2}H^{17}O$	20	$1.122x10^{-5}$	112
$^{2}H^{2}H^{16}O$	20	$2.245x10^{-6}$	22
$^{2}H^{2}H^{18}O$	22	$6x10^{-9}$	0.06
$^{2}H^{2}H^{17}O$	21	$1x10^{-9}$	0.01

Used in Hydrology

Heavy Water

Based on: Millero & Sohn, 1992 Chemical Oceanography, CRC Press; and Gat, 2010 Isotope Hydrology, Imperial College Press

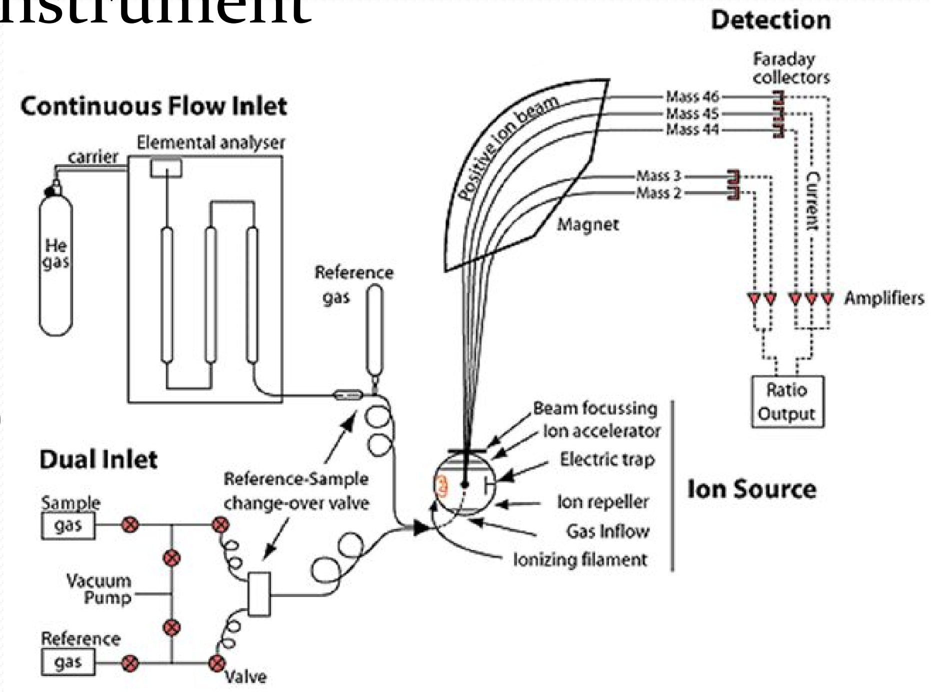
Properties of Stable Water Isotopes

Property	**$^1H^1H^{16}O$**	**$^1H^1H^{18}O$**	**$^1H^2H^{16}O$**	**$^2H^2H^{16}O$**	**units**
Density @30°C		1.107845	1.04945	1.10323	g/mL
Temp@ d_{max}		4.305		11.24	°C
Boiling Pt		100.14		101.42	°C
Melting Pt		0.28		3.81	°C
Diffusivity in water @25°C		2.66		2.34	10^3 cm^2s^{-1}
Relative diffusivity in air	1.0000	0.9723	0.9755		

From: Gat, 2010 Isotope Hydrology, Imperial College Press and references therein

Measurement

- Requires separation of H from O in water
  - Hydrogen goes to H_2 with help of a hot metal catalyst
  - Oxygen goes to O_2 by hydrolysis or fluorination or to CO_2 by aqueous equilibration
- Then use an isotope ratio instrument
  - Magnetic sector Mass Spectrometer
  - Wavelength-Scanned Cavity Ring Down Spectrometer (WS-CRDS)



Relative Isotopic Abundance

- Reflects environmental fractionation
  - Helps describe origins, pathways, processes
  - Tracer
- Calculation based on a standard material
  - Uses ratios of abundance; eg:

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) x1000$$

- Where: R is the isotopic ratio, e.g., for oxygen

$$R = {[{}^{18}O]}\big/{[{}^{16}O]}$$

Fundamentals of Isotope Geochemistry

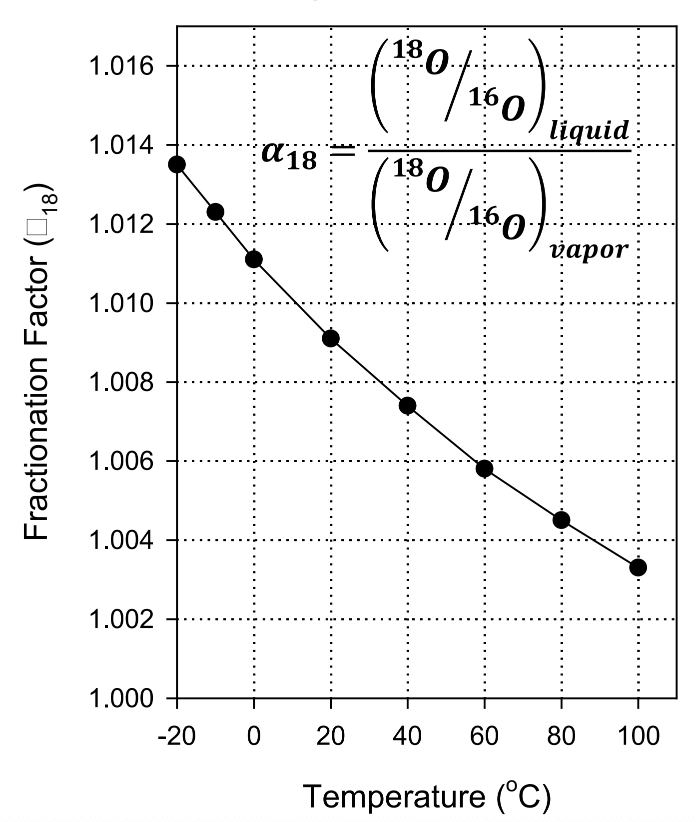
Isotopic Standards in %

Ratio	Nominal	V-SMOW	PDB	
$^{2}H/^{1}H$	0.015	0.015576		
$^{13}C/^{12}C$	1.1		1.12375	
$^{18}O/^{16}O$	0.2	0.20052	0.20672	

- Key to Standards
  - V-SMOW = Vienna Standard Mean Ocean Water
    - established by IAEA in Vienna; blend of ocean waters around globe
  - PDB = PeeDee Belemnite (high $^{13}C/^{12}C$ ratio)
    - Fossilized cephalopods from the PeeDee River in SC

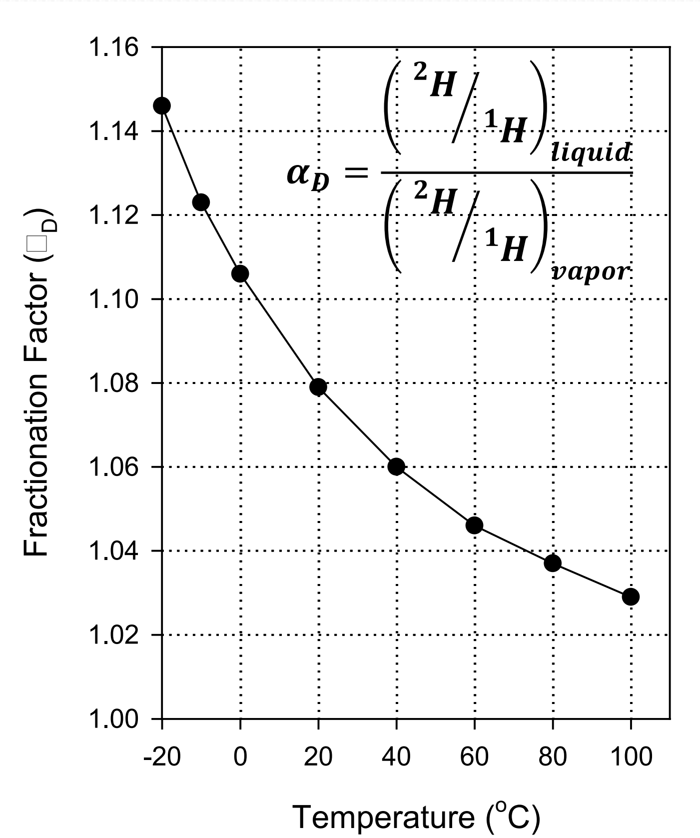
Evaporation of water: fractionation

- For ^{18}O



$$\alpha_{18} = \frac{\left({}^{18}O/{}^{16}O\right)_{liquid}}{\left({}^{18}O/{}^{16}O\right)_{vapor}}$$

- For ^{2}H



$$\alpha_{D} = \frac{\left({}^{2}H/{}^{1}H\right)_{liquid}}{\left({}^{2}H/{}^{1}H\right)_{vapor}}$$

Data from: Dansgaard, 1964

example

- A rainwater sample from Boston has an $^{18}O/^{16}O$ ratio of 0.0019750 as determined by isotope ratio MS.
  1. Calculate the delta value vs V-SMOW (in ‰)

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) x1000 = \left(\frac{0.0019750 - 0.0020052}{0.0020052}\right) x1000 = \mathbf{-15.1}$$

  2. Determine the delta value for the water vapor that is in equilibrium with at 20C

$$\boldsymbol{\alpha_{18}} = \frac{\mathbf{0.0019750}}{\boldsymbol{R_{vapor}}} = \mathbf{1.009}$$

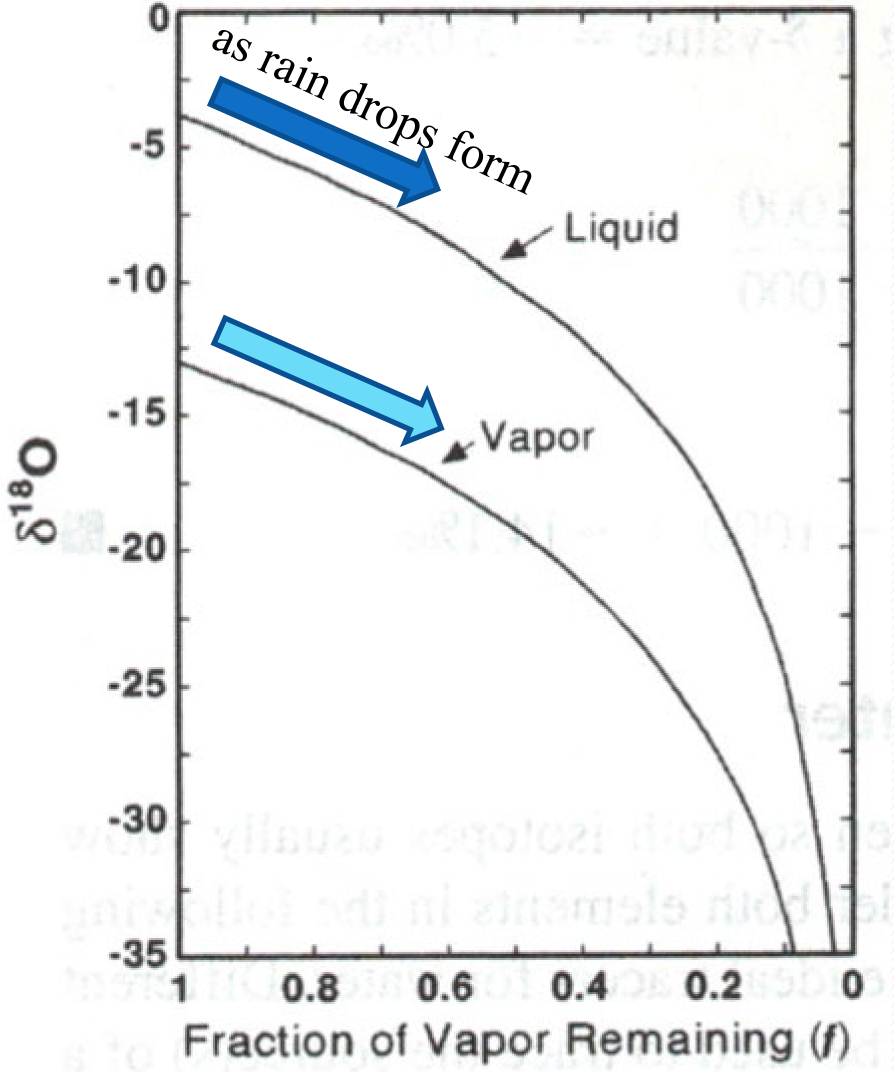
$$\boldsymbol{\alpha_{18}} = \frac{\left({}^{18}\boldsymbol{O}/{}^{16}\boldsymbol{O}\right)_{\boldsymbol{liquid}}}{\left({}^{18}\boldsymbol{O}/{}^{16}\boldsymbol{O}\right)_{\boldsymbol{vapor}}} = \mathbf{1.009}$$

$$R_{vapor} = 0.0019574$$

$$\delta = \left(\frac{0.0019750 - 0.0020052}{0.0020052}\right) x1000 = \mathbf{-23.8}$$

Vapor washout

- Rayleigh distillation
  - Water vapor is enriched in the light isotopes (^{16}O and ^{1}H) compared to the water from which it evaporated
  - As rain drops form there is selective loss of the heavier isotopes (^{18}O and ^{2}H) from the vapor to the rain drops



Selective enrichment in nature

- Mass-based Effects: Fractionation
  - Evaporation & freezing
    - selective concentration of heavy isotopes
- Bonding Effects
  - plants preferentially take up carbon dioxide containing the lighter carbon isotope ($^{12}C-CO_2$) in photosynthesis, but the degree of preference depends on water availability, CO2 availability and on the photosynthetic pathway
  - C3 vs C4 plants (PEP carboxylase)

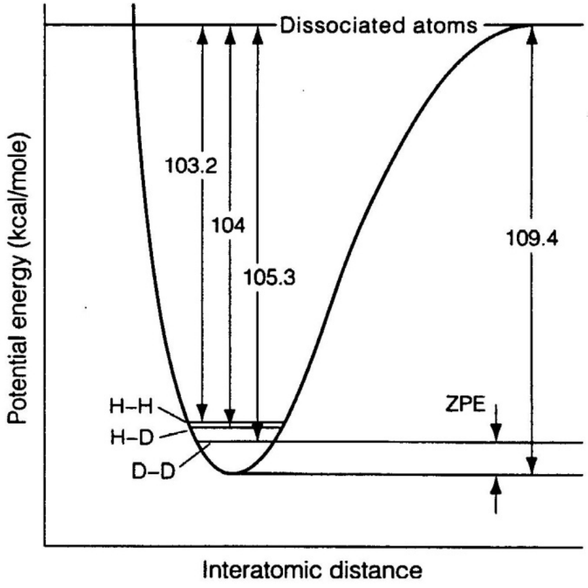


Figure 2.2. The interatomic distance - potential energy relationship for stable hydrogen isotopes of a molecule. Higher zero point energies (ZPE) result in molecules being less stable. Modified from O'Neil (1986).

Radioactive isotopes for dating

- Radioisotope dating

Radio-isotope	Half-life (years)
^{10}Be	1,360,000
^{36}Cl	301,000
^{81}Kr	229,000
^{14}C	5,730
^{39}Ar	269
^{3}H	12
^{85}Kr	11

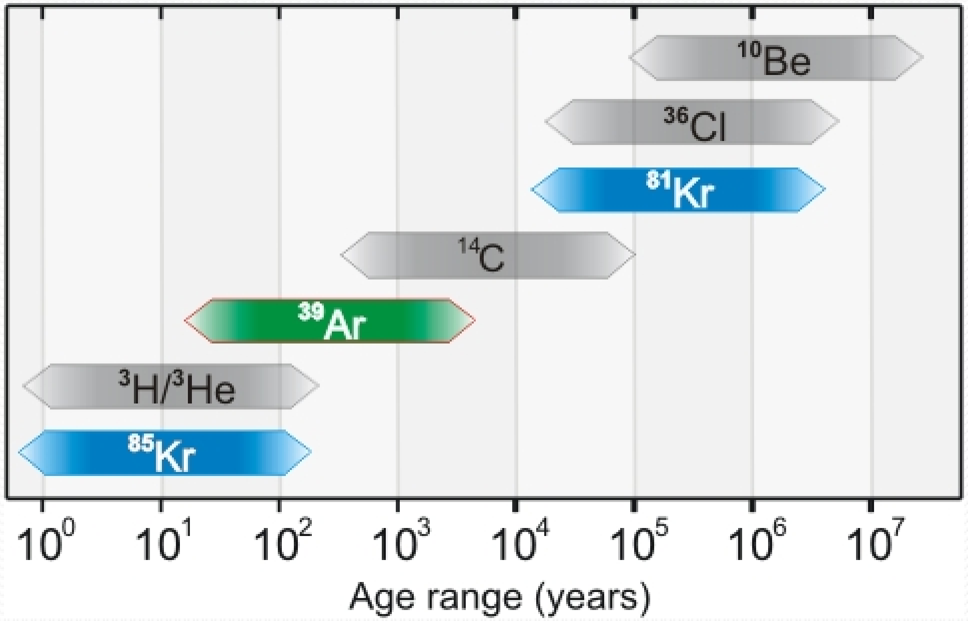
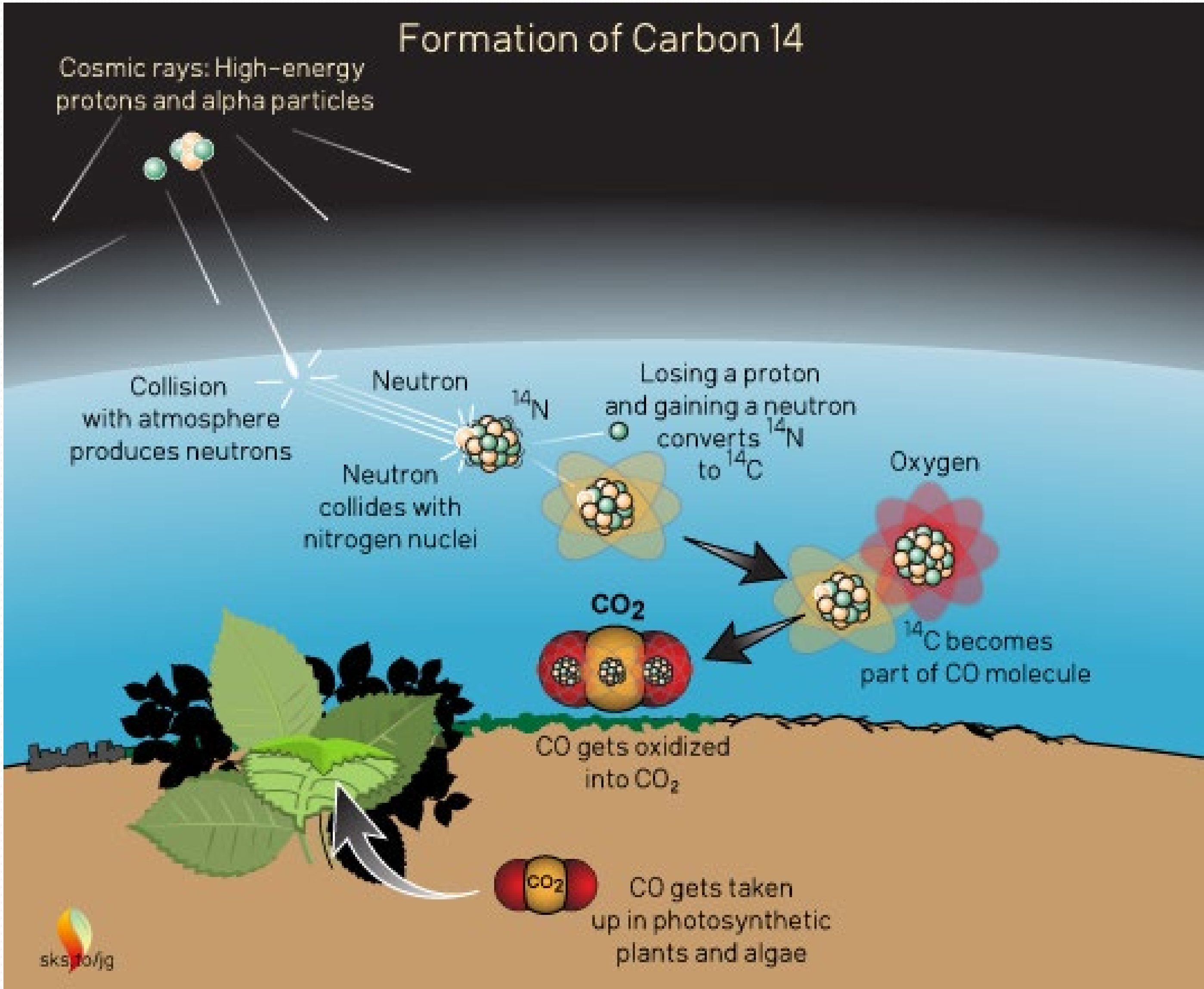


Image from: https://www.phy.anl.gov/mep/atta/research/atta.html

Radioactive tracers

Image from: https://www.skepticalscience.com/print.php?n=3962

- Carbon-14



Molecular Weight and boiling point

- Organic Compounds: Homologous series

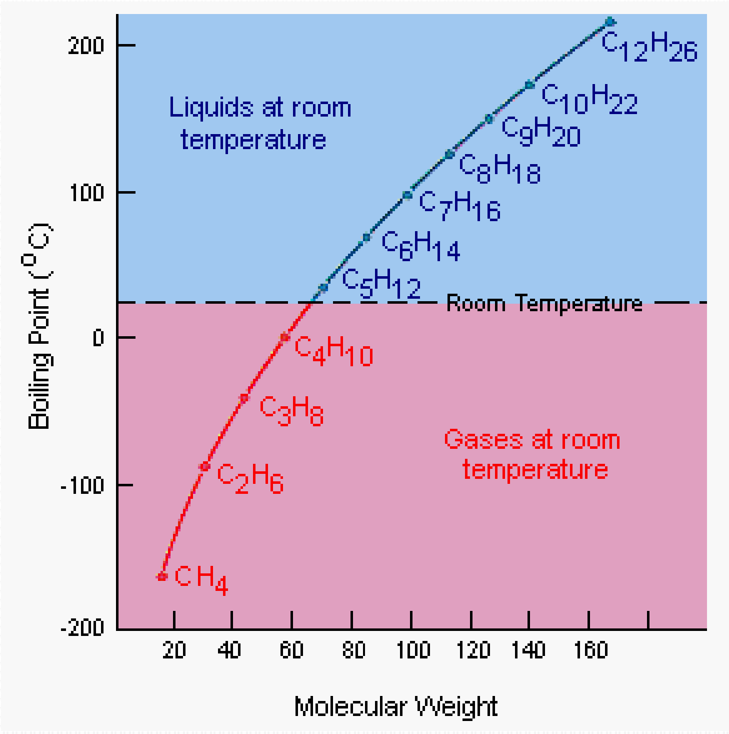


Image from: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch14/liquids.php

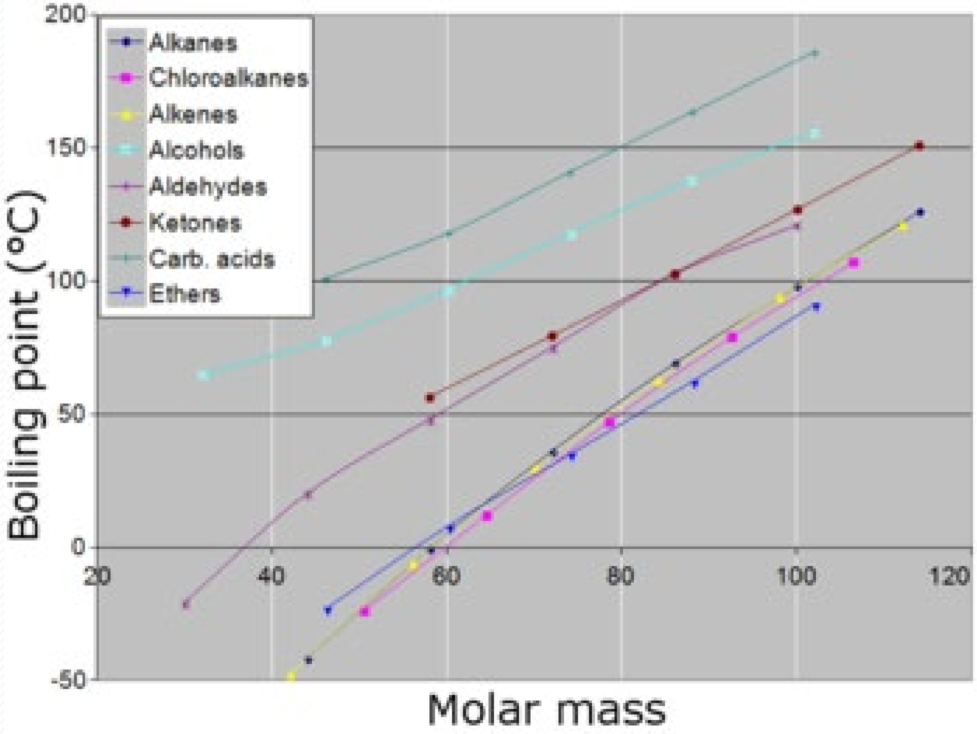
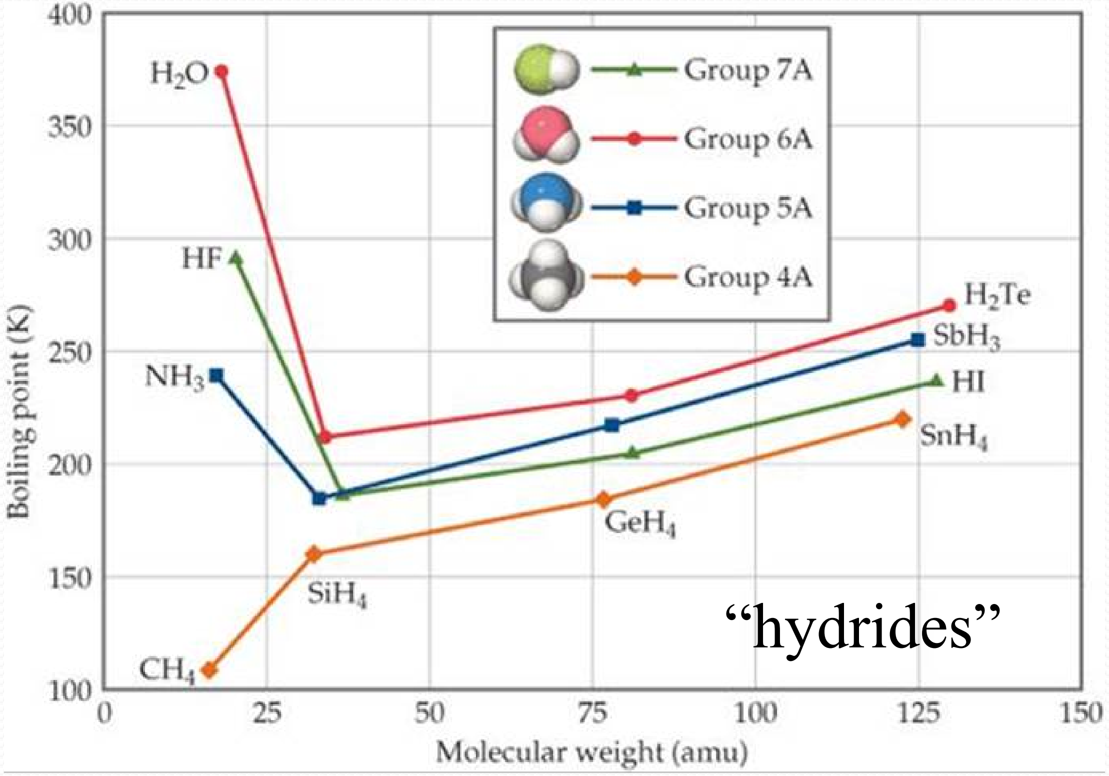


Image from: https://socratic.org/questions/how-does-molar-mass-affect-boiling-point

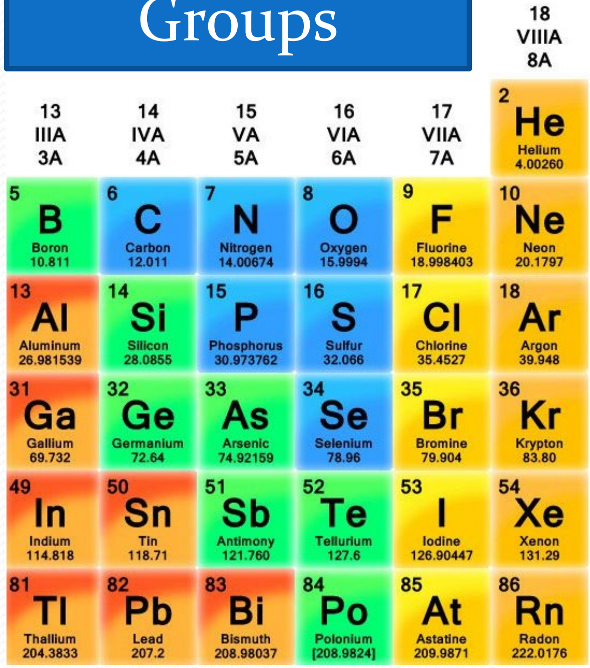
Water and related heteroatoms

- Water is different



“hydrides”

Groups



13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
					2 He Helium 4.00260
5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176

Image From: http://schoolbag.info/chemistry/central/100.html

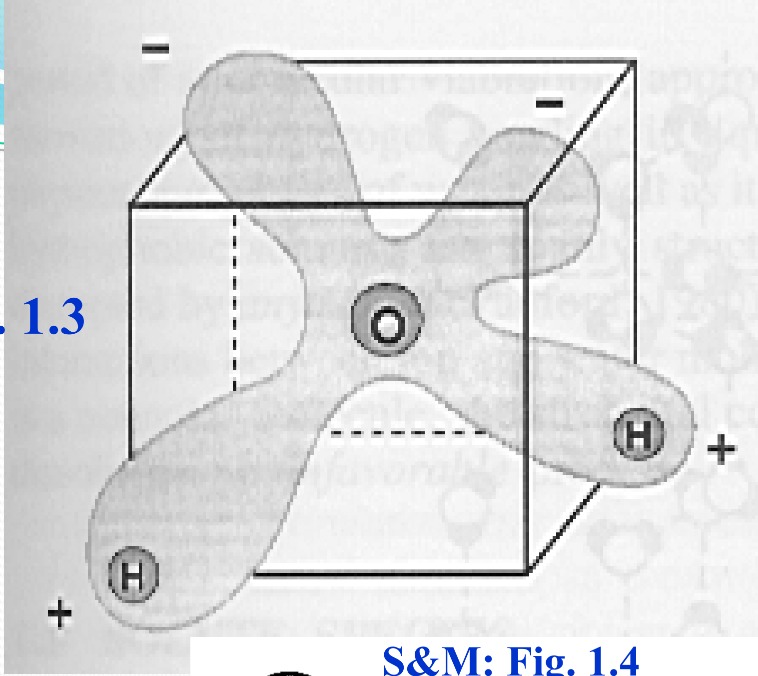
Water is exceptional

- From Eby, 2016 (Table 1-7)

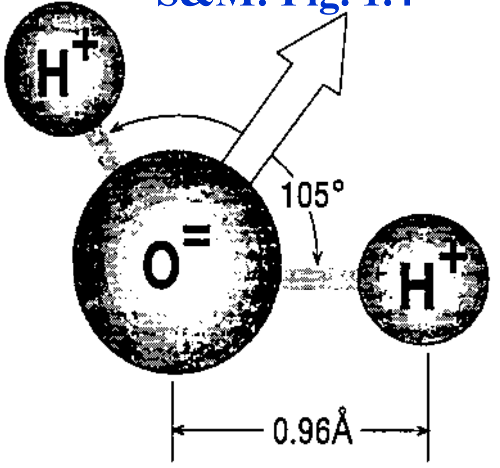
Property	Comparison to other substances
Heat capacity	Highest of all common liquids (except ammonia) and solids
Latent heat of fusion	Highest of all common liquids (except ammonia) and most solids
Latent heat of vaporization	Highest of all common substances
Dissolving ability	Dissolved more substances (particularly ionic compounds), and in greater quantity than any other common liquid
Transparency	Relatively high for visible light
Physical state	The only substance that occurs naturally in all three states at the earth's surface
Surface tension	Highest of all common liquids
Conduction of heat	Highest of all common liquids (Hg is higher)
Viscosity	Relatively low viscosity for a liquid

Structure of Water

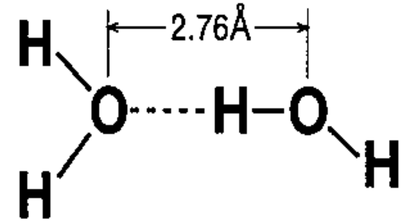
- sp³ hybridization
    - 2 bonding and 2 non-bonding orbitals
- Dipolar Character
- Origin of Water’s Unusual properties
    - High melting and boiling point
    - High heat of vaporization
    - Expands upon freezing
    - High surface tension
    - Excellent polar solvent

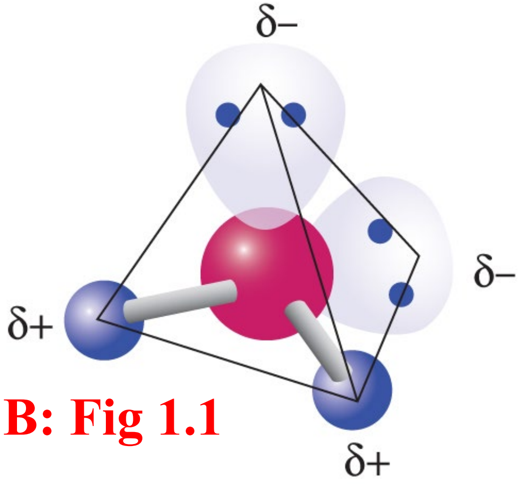


S&M: Fig. 1.3

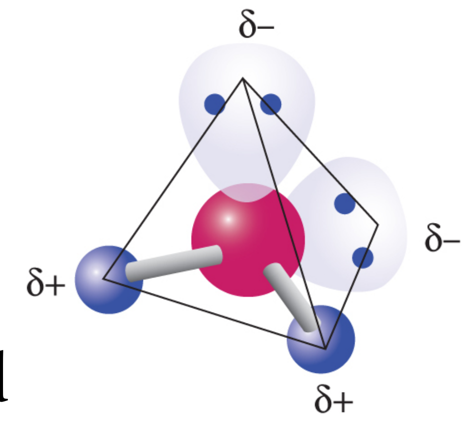


S&M: Fig. 1.4



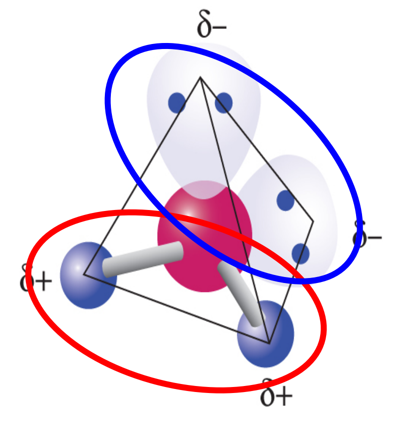


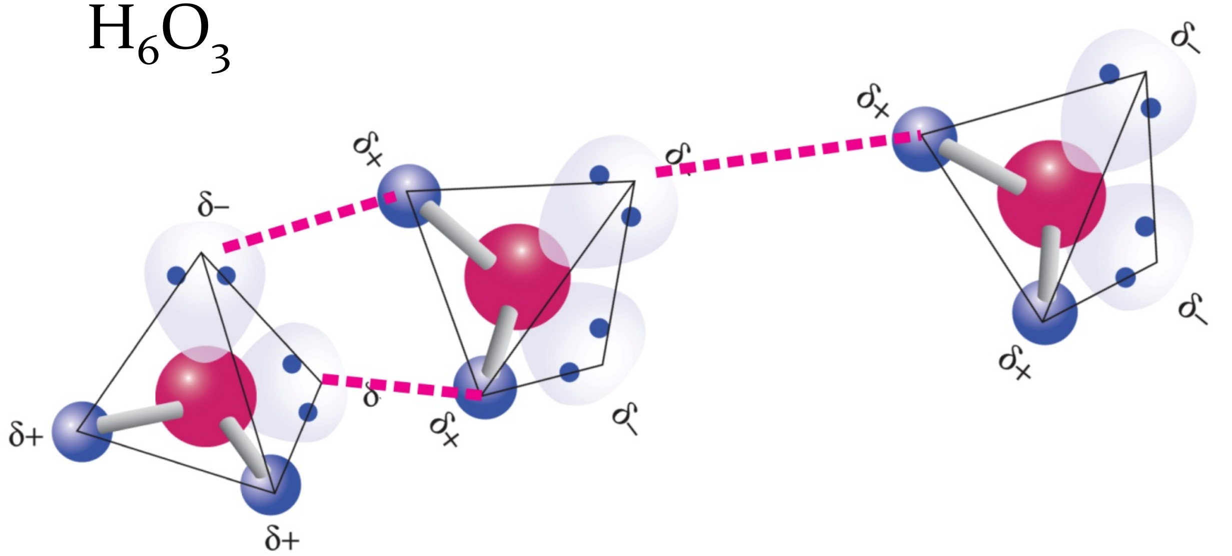
B: Fig 1.1



Hydrogen bonding

- Dipole nature of water and hydrogen bond formation
  - H_2O H_4O_2 H_6O_3





Images courtesy of Benjamin

Water's intermolecular structure

- Dominated by Hydrogen Bonds
- Ice
  - Open tetrahedral structure
- Water
  - Flickering cluster model
    - 100 ps lifetime
    - 0.1 ps molecular vibration

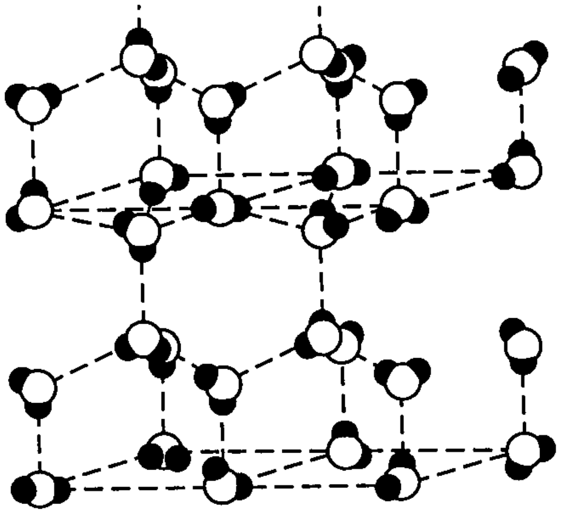


Fig. 1.5a
Pg. 8

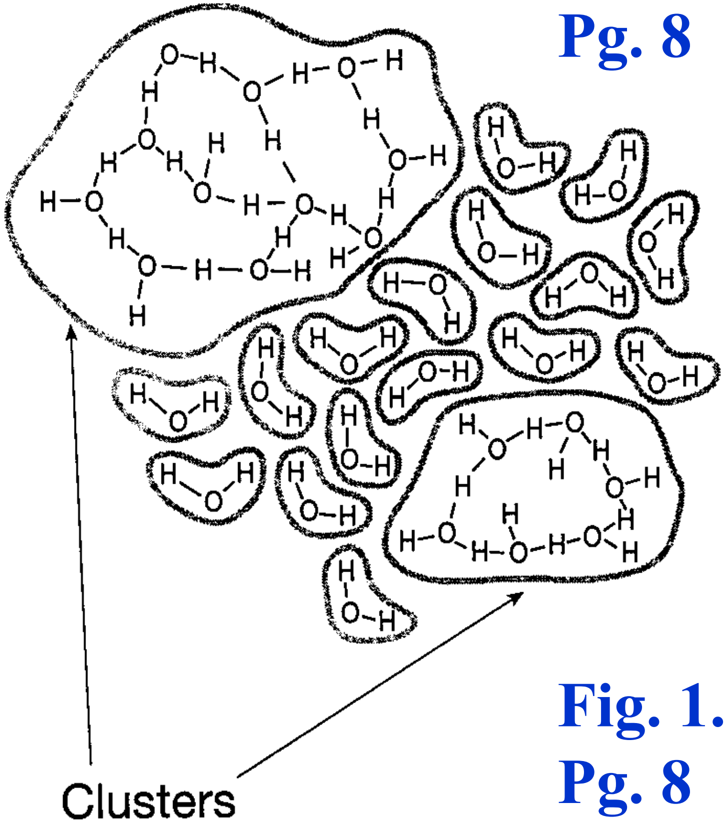


Fig. 1.5b
Pg. 8

Freezing and density

- Crystalline structure
  - Lower density than liquid water
- Max density is at 4°C

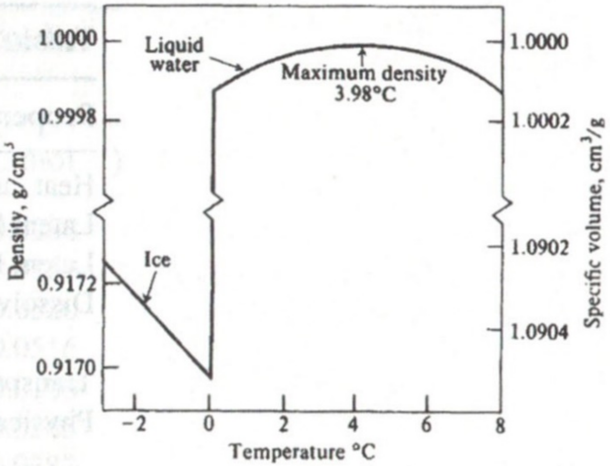
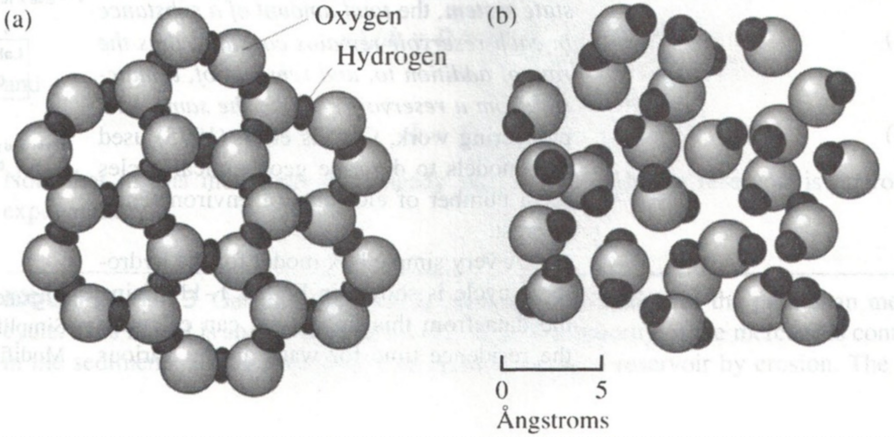


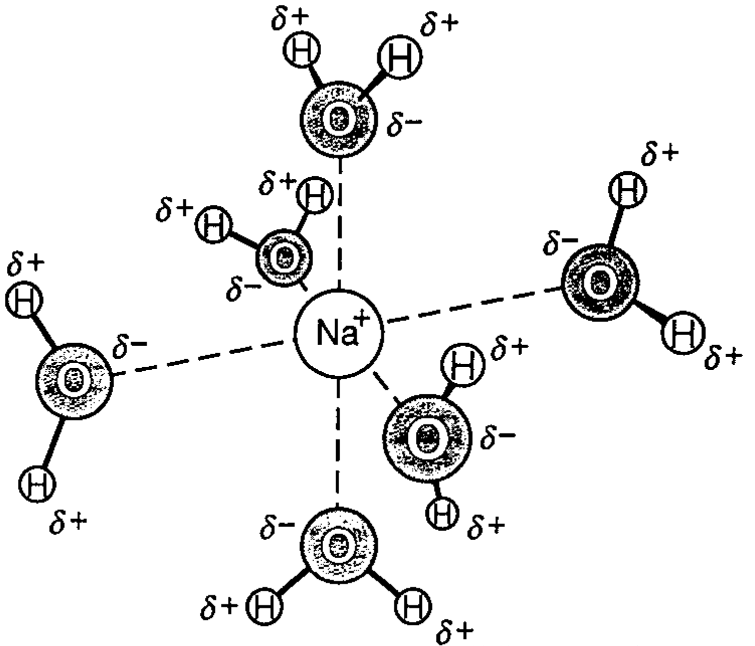
Figure 1–9
Density of pure water near the freezing point. From Duxbury (1971).

Figure 1–8
(a) The crystal structure of ice showing the six-sided rings formed by 24 water molecules. (b) The structure of liquid water. In the same volume of liquid water, there are 27 water molecules; hence, liquid water has a greater density than ice. From Gross and Gross (1996).



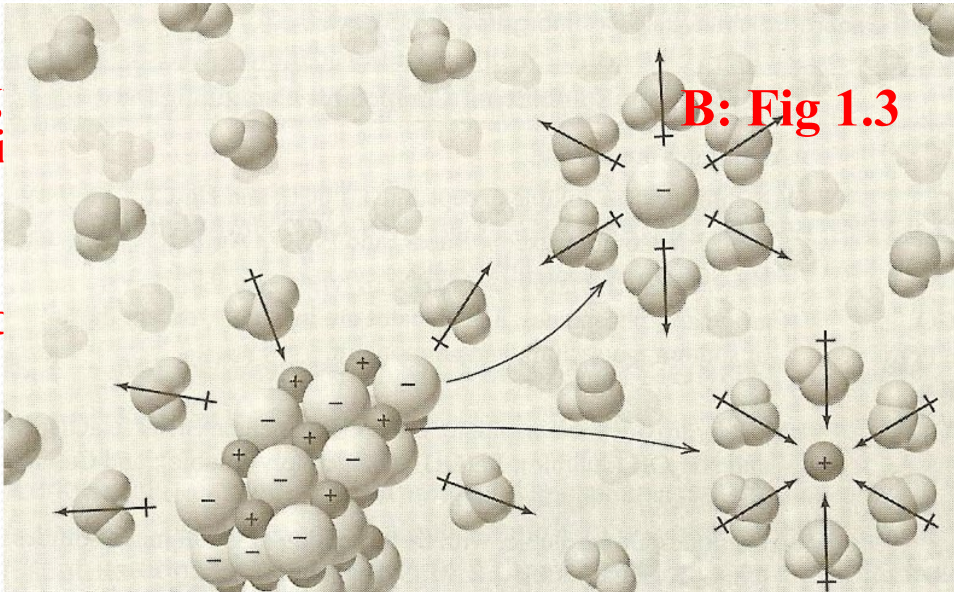
Images from Eby, 2016

Solutes in Water



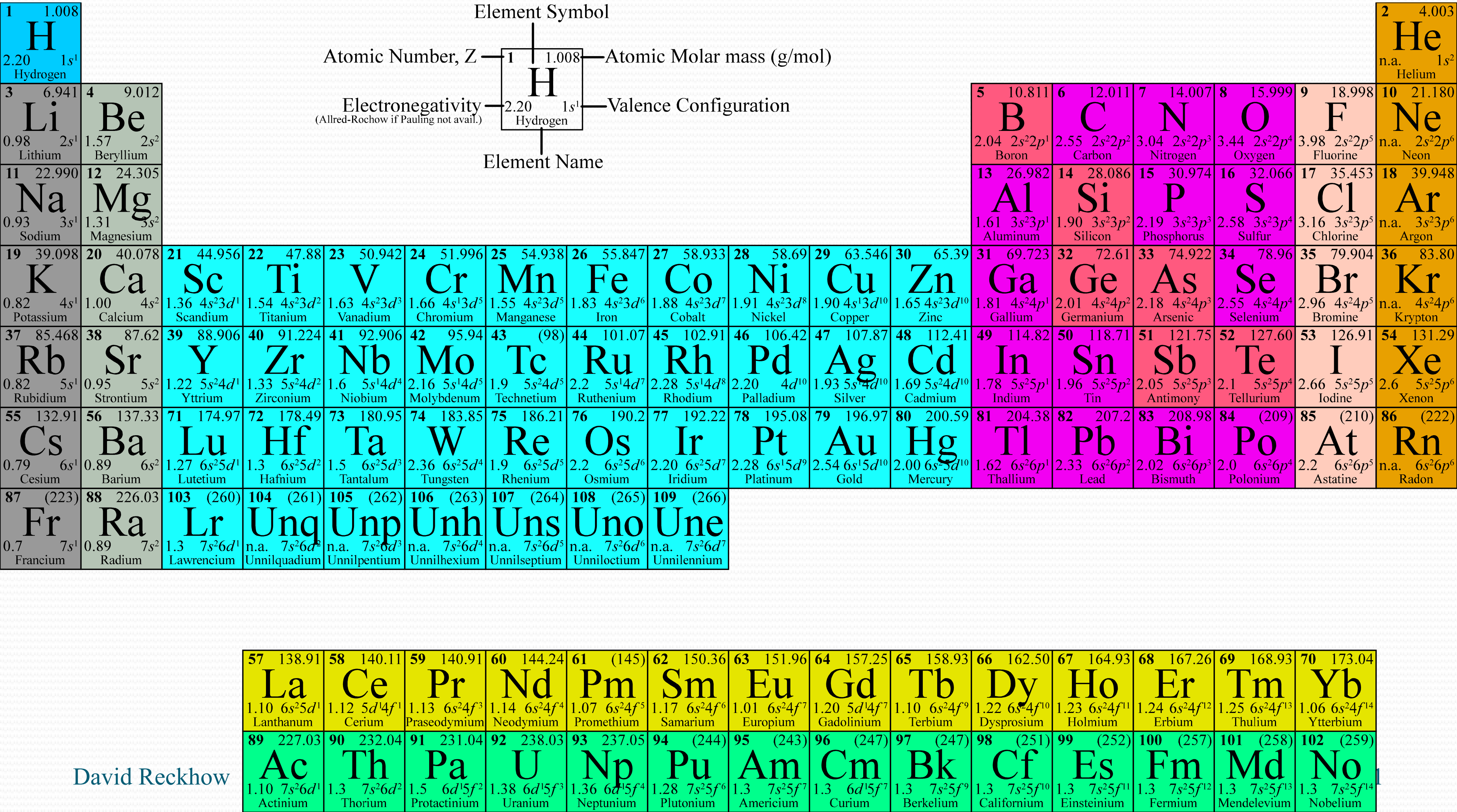
S&M: Fig. 1.6

- Great solvent for ionic or ionizable substances
- Ion-dipole bonds improves stability
  - Energy increases with charge of ion and decreases with size
  - Solvent hole model
    - As solute-water bonding streng compared to water-water bondi solubility goes up
      - Hydrophilic solute
    - Weak solute-water bonds reduc solubility
      - Hydrophobic solutes



B: Fig 1.3

Periodic Table



Element Symbol
Atomic Number, Z
Atomic Molar mass (g/mol)
Electronegativity
(Allred-Rochow if Pauling not avail.)
Valence Configuration
Element Name

1 1.008
H
2.20 $1s^1$
Hydrogen

1 1.008 H 2.20 $1s^1$ Hydrogen																	2 4.003 He n.a. $1s^2$ Helium
3 6.941 Li 0.98 $2s^1$ Lithium	4 9.012 Be 1.57 $2s^2$ Beryllium											5 10.811 B 2.04 $2s^2 2p^1$ Boron	6 12.011 C 2.55 $2s^2 2p^2$ Carbon	7 14.007 N 3.04 $2s^2 2p^3$ Nitrogen	8 15.999 O 3.44 $2s^2 2p^4$ Oxygen	9 18.998 F 3.98 $2s^2 2p^5$ Fluorine	10 21.180 Ne n.a. $2s^2 2p^6$ Neon
11 22.990 Na 0.93 $3s^1$ Sodium	12 24.305 Mg 1.31 $3s^2$ Magnesium											13 26.982 Al 1.61 $3s^2 3p^1$ Aluminum	14 28.086 Si 1.90 $3s^2 3p^2$ Silicon	15 30.974 P 2.19 $3s^2 3p^3$ Phosphorus	16 32.066 S 2.58 $3s^2 3p^4$ Sulfur	17 35.453 Cl 3.16 $3s^2 3p^5$ Chlorine	18 39.948 Ar n.a. $3s^2 3p^6$ Argon
19 39.098 K 0.82 $4s^1$ Potassium	20 40.078 Ca 1.00 $4s^2$ Calcium	21 44.956 Sc 1.36 $4s^2 3d^1$ Scandium	22 47.88 Ti 1.54 $4s^2 3d^2$ Titanium	23 50.942 V 1.63 $4s^2 3d^3$ Vanadium	24 51.996 Cr 1.66 $4s^1 3d^5$ Chromium	25 54.938 Mn 1.55 $4s^2 3d^5$ Manganese	26 55.847 Fe 1.83 $4s^2 3d^6$ Iron	27 58.933 Co 1.88 $4s^2 3d^7$ Cobalt	28 58.69 Ni 1.91 $4s^2 3d^8$ Nickel	29 63.546 Cu 1.90 $4s^1 3d^{10}$ Copper	30 65.39 Zn 1.65 $4s^2 3d^{10}$ Zinc	31 69.723 Ga 1.81 $4s^2 4p^1$ Gallium	32 72.61 Ge 2.01 $4s^2 4p^2$ Germanium	33 74.922 As 2.18 $4s^2 4p^3$ Arsenic	34 78.96 Se 2.55 $4s^2 4p^4$ Selenium	35 79.904 Br 2.96 $4s^2 4p^5$ Bromine	36 83.80 Kr n.a. $4s^2 4p^6$ Krypton
37 85.468 Rb 0.82 $5s^1$ Rubidium	38 87.62 Sr 0.95 $5s^2$ Strontium	39 88.906 Y 1.22 $5s^2 4d^1$ Yttrium	40 91.224 Zr 1.33 $5s^2 4d^2$ Zirconium	41 92.906 Nb 1.6 $5s^1 4d^4$ Niobium	42 95.94 Mo 2.16 $5s^1 4d^5$ Molybdenum	43 (98) Tc 1.9 $5s^2 4d^5$ Technetium	44 101.07 Ru 2.2 $5s^1 4d^7$ Ruthenium	45 102.91 Rh 2.28 $5s^1 4d^8$ Rhodium	46 106.42 Pd 2.20 $4d^{10}$ Palladium	47 107.87 Ag 1.93 $5s^1 4d^{10}$ Silver	48 112.41 Cd 1.69 $5s^2 4d^{10}$ Cadmium	49 114.82 In 1.78 $5s^2 5p^1$ Indium	50 118.71 Sn 1.96 $5s^2 5p^2$ Tin	51 121.75 Sb 2.05 $5s^2 5p^3$ Antimony	52 127.60 Te 2.1 $5s^2 5p^4$ Tellurium	53 126.91 I 2.66 $5s^2 5p^5$ Iodine	54 131.29 Xe 2.6 $5s^2 5p^6$ Xenon
55 132.91 Cs 0.79 $6s^1$ Cesium	56 137.33 Ba 0.89 $6s^2$ Barium	71 174.97 Lu 1.27 $6s^2 5d^1$ Lutetium	72 178.49 Hf 1.3 $6s^2 5d^2$ Hafnium	73 180.95 Ta 1.5 $6s^2 5d^3$ Tantalum	74 183.85 W 2.36 $6s^2 5d^4$ Tungsten	75 186.21 Re 1.9 $6s^2 5d^5$ Rhenium	76 190.2 Os 2.2 $6s^2 5d^6$ Osmium	77 192.22 Ir 2.20 $6s^2 5d^7$ Iridium	78 195.08 Pt 2.28 $6s^1 5d^9$ Platinum	79 196.97 Au 2.54 $6s^1 5d^{10}$ Gold	80 200.59 Hg 2.00 $6s^2 5d^{10}$ Mercury	81 204.38 Tl 1.62 $6s^2 6p^1$ Thallium	82 207.2 Pb 2.33 $6s^2 6p^2$ Lead	83 208.98 Bi 2.02 $6s^2 6p^3$ Bismuth	84 (209) Po 2.0 $6s^2 6p^4$ Polonium	85 (210) At 2.2 $6s^2 6p^5$ Astatine	86 (222) Rn n.a. $6s^2 6p^6$ Radon
87 (223) Fr 0.7 $7s^1$ Francium	88 226.03 Ra 0.89 $7s^2$ Radium	103 (260) Lr 1.3 $7s^2 6d^1$ Lawrencium	104 (261) Unq n.a. $7s^2 6d^2$ Unnilquadium	105 (262) Unp n.a. $7s^2 6d^3$ Unnilpentium	106 (263) Unh n.a. $7s^2 6d^4$ Unnilhexium	107 (264) Uns n.a. $7s^2 6d^5$ Unnilseptium	108 (265) Uno n.a. $7s^2 6d^6$ Unniloctium	109 (266) Une n.a. $7s^2 6d^7$ Unnilennium									
			57 138.91 La 1.10 $6s^2 5d^1$ Lanthanum	58 140.11 Ce 1.12 $5d^1 4f^1$ Cerium	59 140.91 Pr 1.13 $6s^2 4f^3$ Praseodymium	60 144.24 Nd 1.14 $6s^2 4f^4$ Neodymium	61 (145) Pm 1.07 $6s^2 4f^5$ Promethium	62 150.36 Sm 1.17 $6s^2 4f^6$ Samarium	63 151.96 Eu 1.01 $6s^2 4f^7$ Europium	64 157.25 Gd 1.20 $5d^1 4f^7$ Gadolinium	65 158.93 Tb 1.10 $6s^2 4f^9$ Terbium	66 162.50 Dy 1.22 $6s^2 4f^{10}$ Dysprosium	67 164.93 Ho 1.23 $6s^2 4f^{11}$ Holmium	68 167.26 Er 1.24 $6s^2 4f^{12}$ Erbium	69 168.93 Tm 1.25 $6s^2 4f^{13}$ Thulium	70 173.04 Yb 1.06 $6s^2 4f^{14}$ Ytterbium	
			89 227.03 Ac 1.10 $7s^2 6d^1$ Actinium	90 232.04 Th 1.3 $7s^2 6d^2$ Thorium	91 231.04 Pa 1.5 $6d^1 5f^2$ Protactinium	92 238.03 U 1.38 $6d^1 5f^3$ Uranium	93 237.05 Np 1.36 $6d^1 5f^4$ Neptunium	94 (244) Pu 1.28 $7s^2 5f^6$ Plutonium	95 (243) Am 1.3 $7s^2 5f^7$ Americium	96 (247) Cm 1.3 $6d^1 5f^7$ Curium	97 (247) Bk 1.3 $7s^2 5f^9$ Berkelium	98 (251) Cf 1.3 $7s^2 5f^{10}$ Californium	99 (252) Es 1.3 $7s^2 5f^{11}$ Einsteinium	100 (257) Fm 1.3 $7s^2 5f^{12}$ Fermium	101 (258) Md 1.3 $7s^2 5f^{13}$ Mendelevium	102 (259) No 1.3 $7s^2 5f^{14}$ Nobelium	

"680 Periodic Table"

H 4.5 H_2O -1.74 -1.74							**He** 8.8
Li 6.3 Li^+ 4.6	**Be** $BeOH^+$ (?) 9.2	**B** 7.0 H_3BO_4 3.39	**C** 4.9 HCO_3^- 2.64 3.0	**N** 6.3 N_2, NO_3^- 1.97	**O** 4.5 H_2O, O_2 -1.74 -1.74	**F** 5.7 F^-, MgF^+ 4.17 5.3	**Ne** 8.15
Na 7.7 Na^+ 0.33 3.57	**Mg** 7 Mg^{+2}, $MgSO_4$ 1.27 3.77	**Al** 2 $Al(OH)_4^-$ 7.1	**Si** 3.8 H_4SiO_4 4.15 3.8	**P** 4 HPO_4^{-2} 5.3	**S** 6.9 SO_4^{-2},$NaSO_4^-$ 1.55 3.92	**Cl** 7.9 Cl^- 0.26 3.66	**Ar** 6.96
K 6.7 K^+ 1.99 4.23	**Ca** 5.9 Ca^{+2}, $CaSO_4$ 1.99 3.42			**As** $HAsO_4^{-2}$ 7.3	**Se** 4 SeO_3^{-2} 8.6	**Br** 8 Br^- 3.08	**Kr** 8.6
	Sr 6.6 Sr^{+2} 4.05					**I** 6 I^-, IO_3^- 6.3	
	Ba 4.5 Ba^{+2} 6.8						

- Ocean residence time (log yr)
- Predominant species
- River Water conc. (-log M)
- Seawater conc. (-log M)

After S&M:Fig. 1.7, Pg. 10

Law of Mass Action

- The rate of an elementary reaction is proportional to the product of the concentrations of the participating molecules, atoms or ions
- Chemical equilibria comes from the combination of two competing rates
  - Consider the autodecomposition of water

$$H_2O \leftrightarrow H^+ + OH^-$$

Equilibrium Quotients

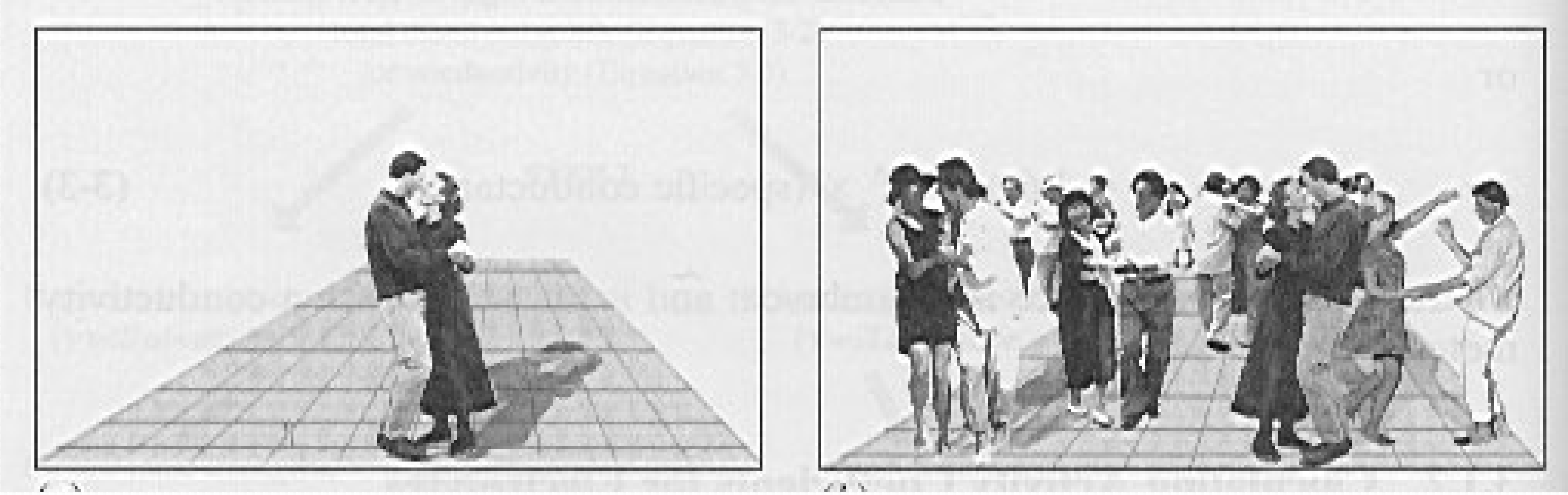
- Other examples
  - acid dissociation, Precipitation, Redox, Adsorption, volatilization

Activity

- Activity is the "effective" concentration or "reactivity", which may be slightly different from the true "analytical" concentration
  - These two differ substantially in waters with high TDS, such as sea water.
- We identify these two as follows:
  - Curved brackets ({X}) indicate activity
  - Square brackets ([X]) indicate concentration
    - Usually this is molar concentration
    - This may also be used when we're not very concerned about the differences between activity and concentration

Why the difference?

- Mostly long-range interactions between uninterested bystanders (chemical species that are not involved in the reaction) and the two dancers of interest (those species that are reacting)



- Relative importance in determining activity
  - Concentration >> charge > polarity > MW

Activity & Ionic Strength

- Equilibrium quotients are really written for activities, not concentrations
- in most natural waters activities are nearly equal to the molar concentrations
- In saline waters, we must account for differences between the two
  - activity coefficients (f or γ) are used for this
  - Ionic Strength (I) is used to determine the extent of correction

$$K = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

$$\{A\} \approx [A]$$

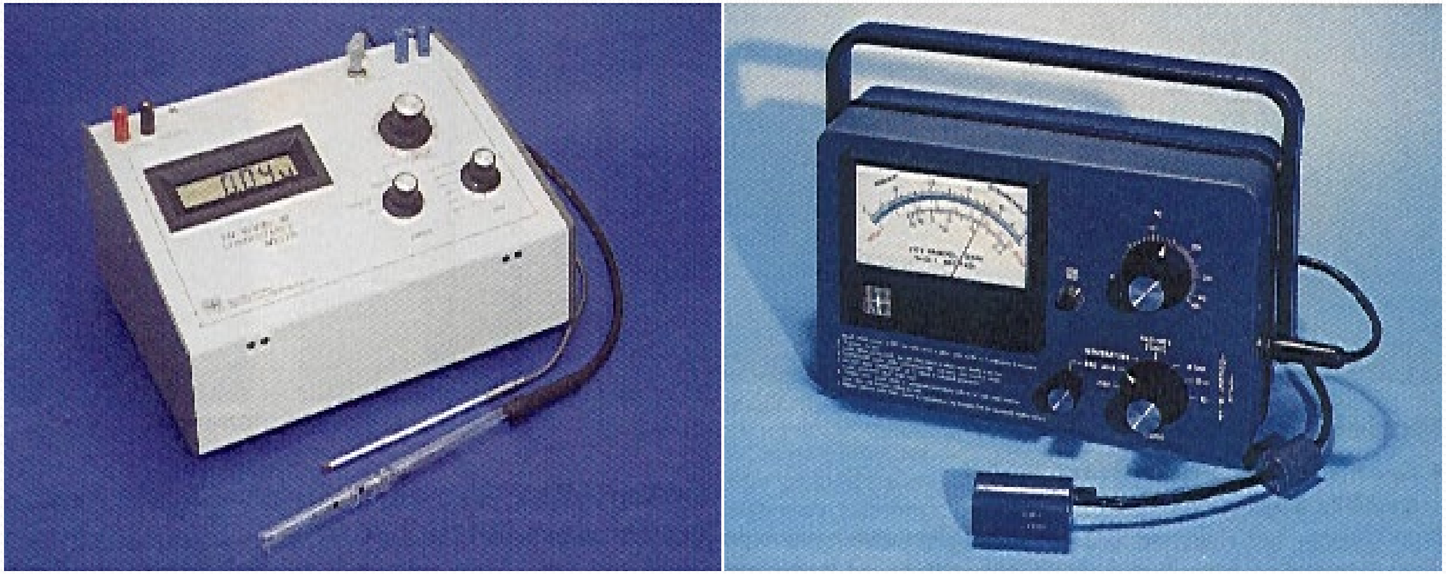
$$\{A\} = f_A [A]$$

$$\{A\} = \gamma_A [A]$$

$$I = \tfrac{1}{2} \sum m_i z_i^2$$

Correlations for ionic strength

- μ vs. specific conductance: Russell Approximation
  - $\mu = 1.6 \times 10^{-5} \times K$ (in µmho/cm)
- μ vs. TDS: Langlier approximation
  - $\mu \sim 2.5 \times 10^{-5} \times TDS$ (in mg/L)



Equilibrium Constants

- Consider a simple acid/base reaction
  - HA = H^+ + A^-
- The activity-based constant is:
- The concentration-based constant is:
- And a mixed constant would be:

$$K = \frac{\{H^+\}\{A^-\}}{\{HA\}} = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}} = \left(\frac{[H^+][A^-]}{[HA]}\right)\left(\frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}\right)$$

$$^{c}K = K\left(\frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}}\right) = \left(\frac{[H^+][A^-]}{[HA]}\right)$$

$$K' = K\left(\frac{\gamma_{HA}}{\gamma_{A^-}}\right) = \left(\frac{\{H^+\}[A^-]}{[HA]}\right)$$

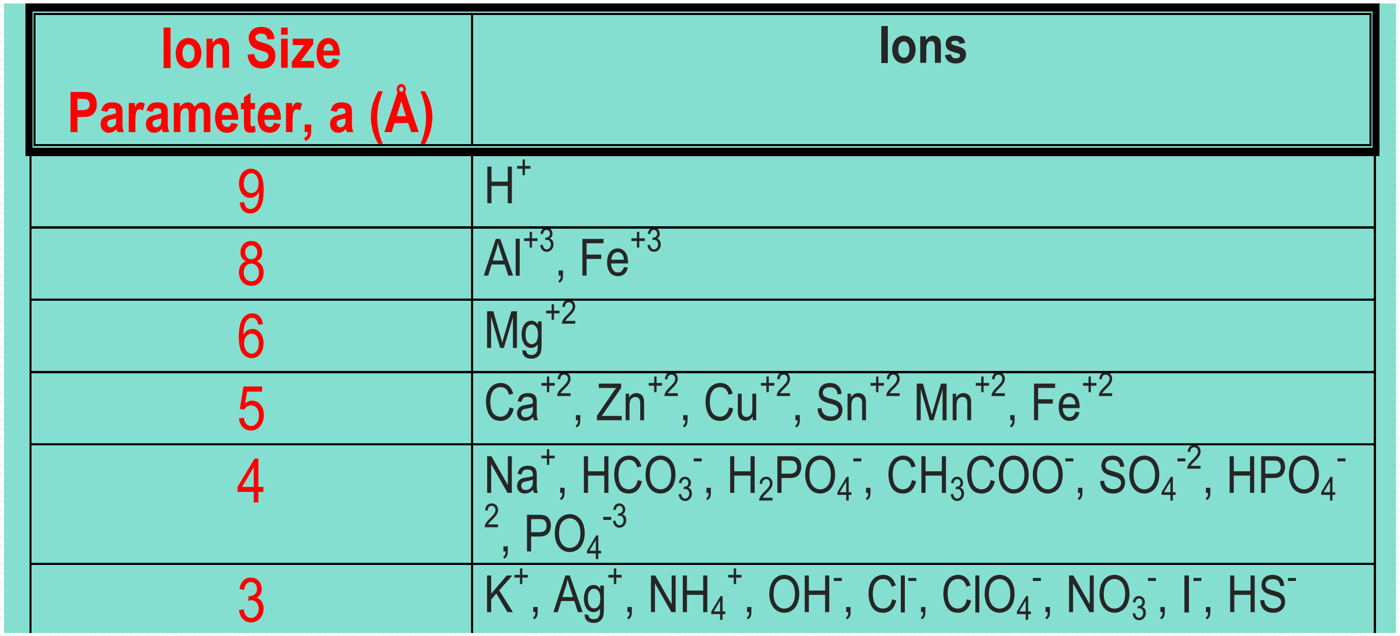
Corrections to Ion Activity

Approximation	Equation	Applicable Range for I
Simple Debye-Hückel	$\log f = -0.5z^2\sqrt{I}$	$<10^{-2.3}$
Extended Debye-Hückel	$\log f = -0.5z^2 \dfrac{\sqrt{I}}{1+0.33a\sqrt{I}}$	$<10^{-1}$
Güntelberg	$\log f = -0.5z^2 \dfrac{\sqrt{I}}{1+\sqrt{I}}$	$<10^{-1}$, solutions of multiple electrolytes
Davies	$\log f = -0.5z^2\left(\dfrac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right)$	<0.5

Based on: S&M, Table 3.3; B, Table 1.4a

note: Mihelcic cites 0.3

Ion Size Parameter

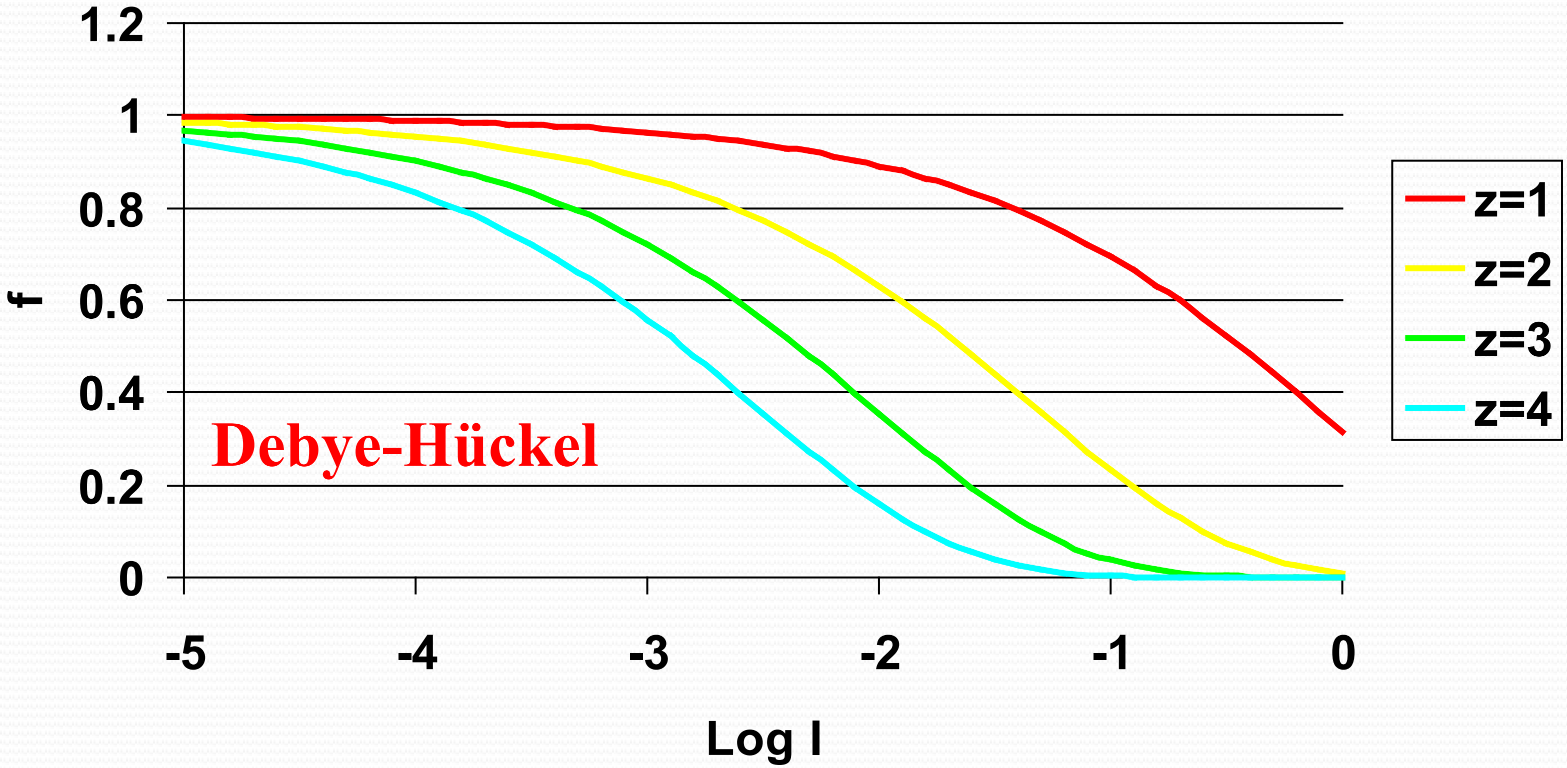


Ion Size Parameter, a (Å)	**Ions**
9	H^+
8	Al^{+3}, Fe^{+3}
6	Mg^{+2}
5	Ca^{+2}, Zn^{+2}, Cu^{+2}, Sn^{+2} Mn^{+2}, Fe^{+2}
4	Na^+, HCO_3^-, $H_2PO_4^-$, CH_3COO^-, SO_4^{-2}, HPO_4^{-2}, PO_4^{-3}
3	K^+, Ag^+, NH_4^+, OH^-, Cl^-, ClO_4^-, NO_3^-, I^-, HS^-

See also: B, Table 1.4b

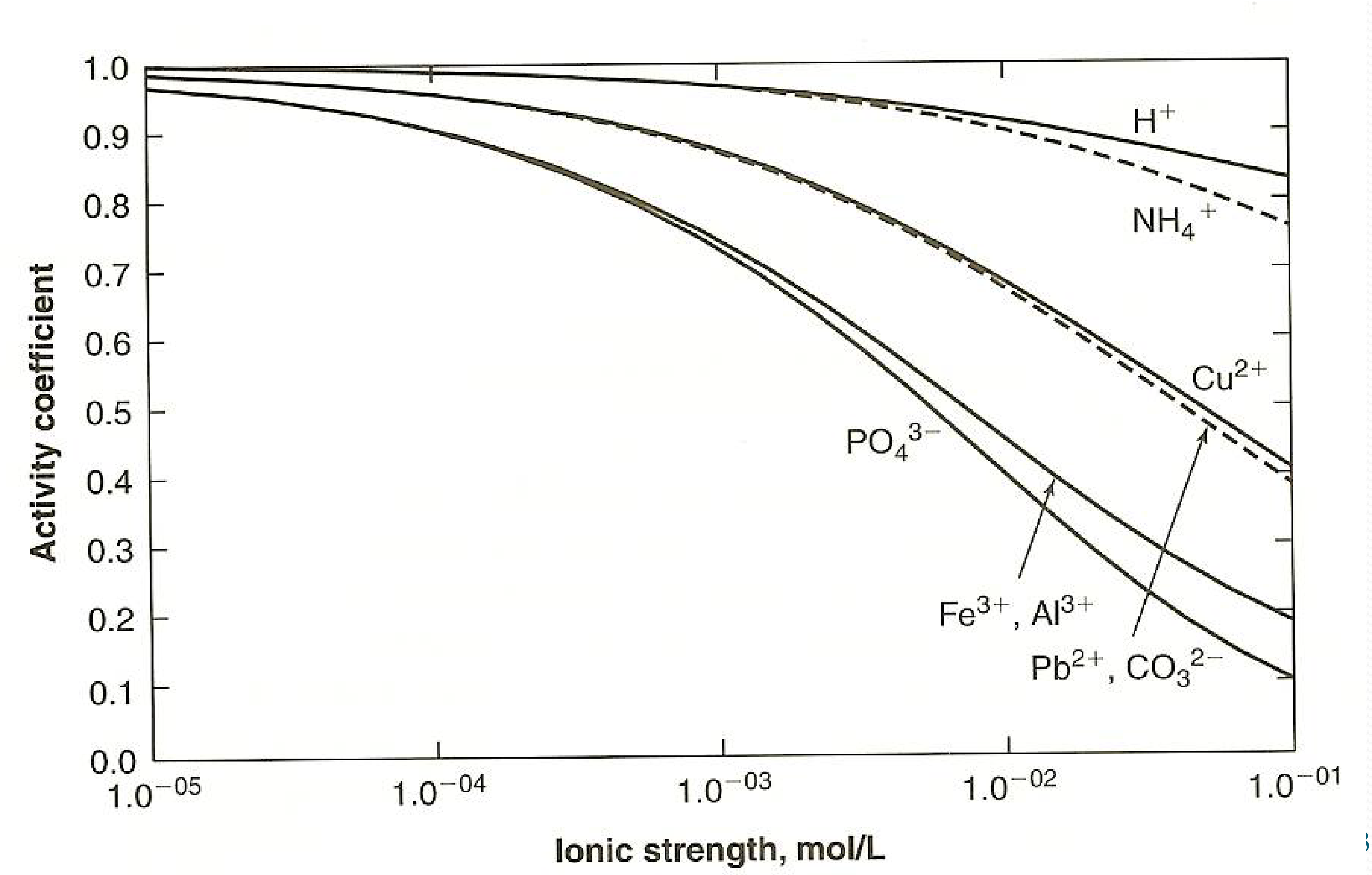
Debye-Hückel

- Effect of charge (z)



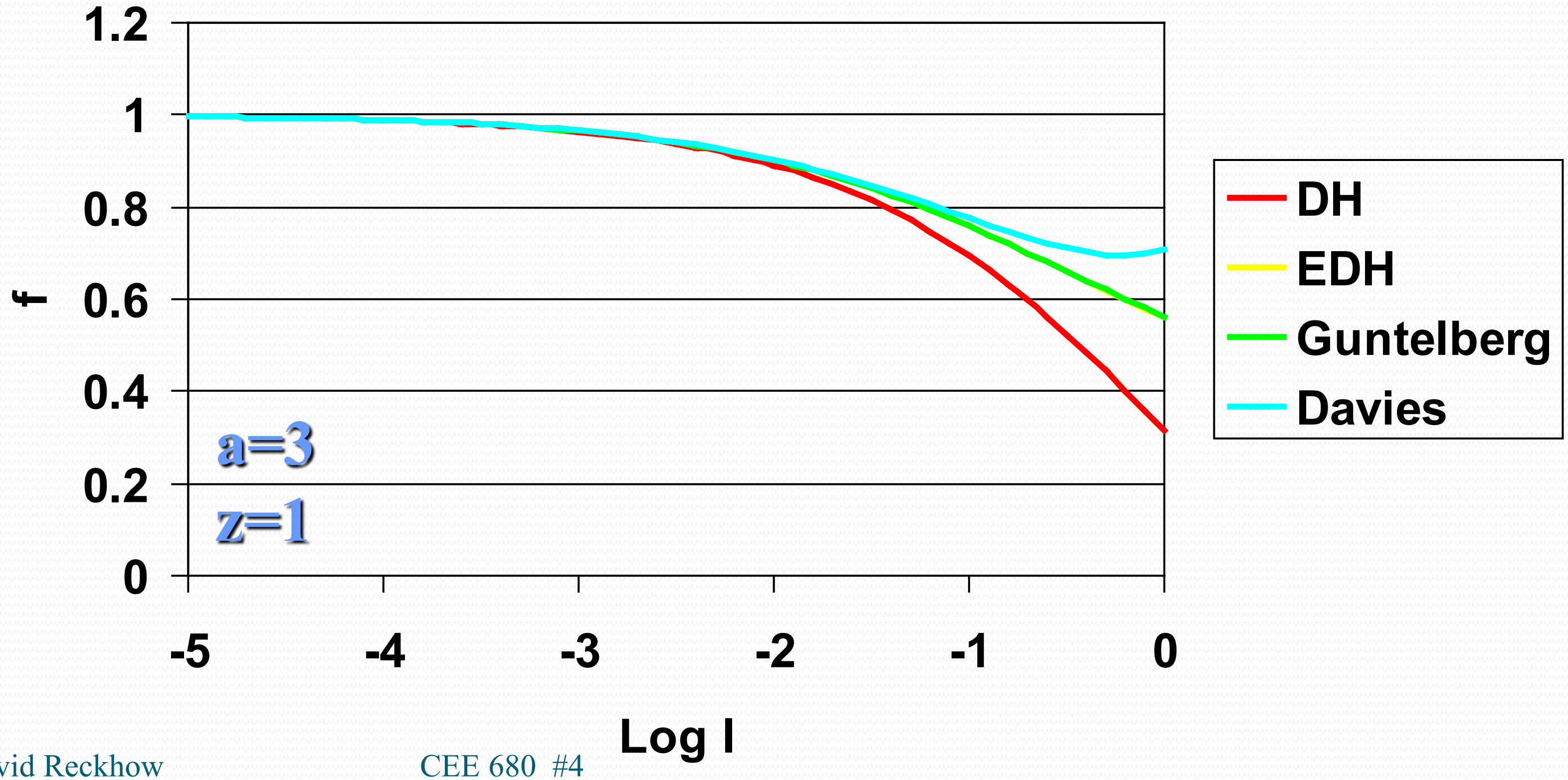
Extended Debye-Hückel

- Benjamin: Figure 1.6a



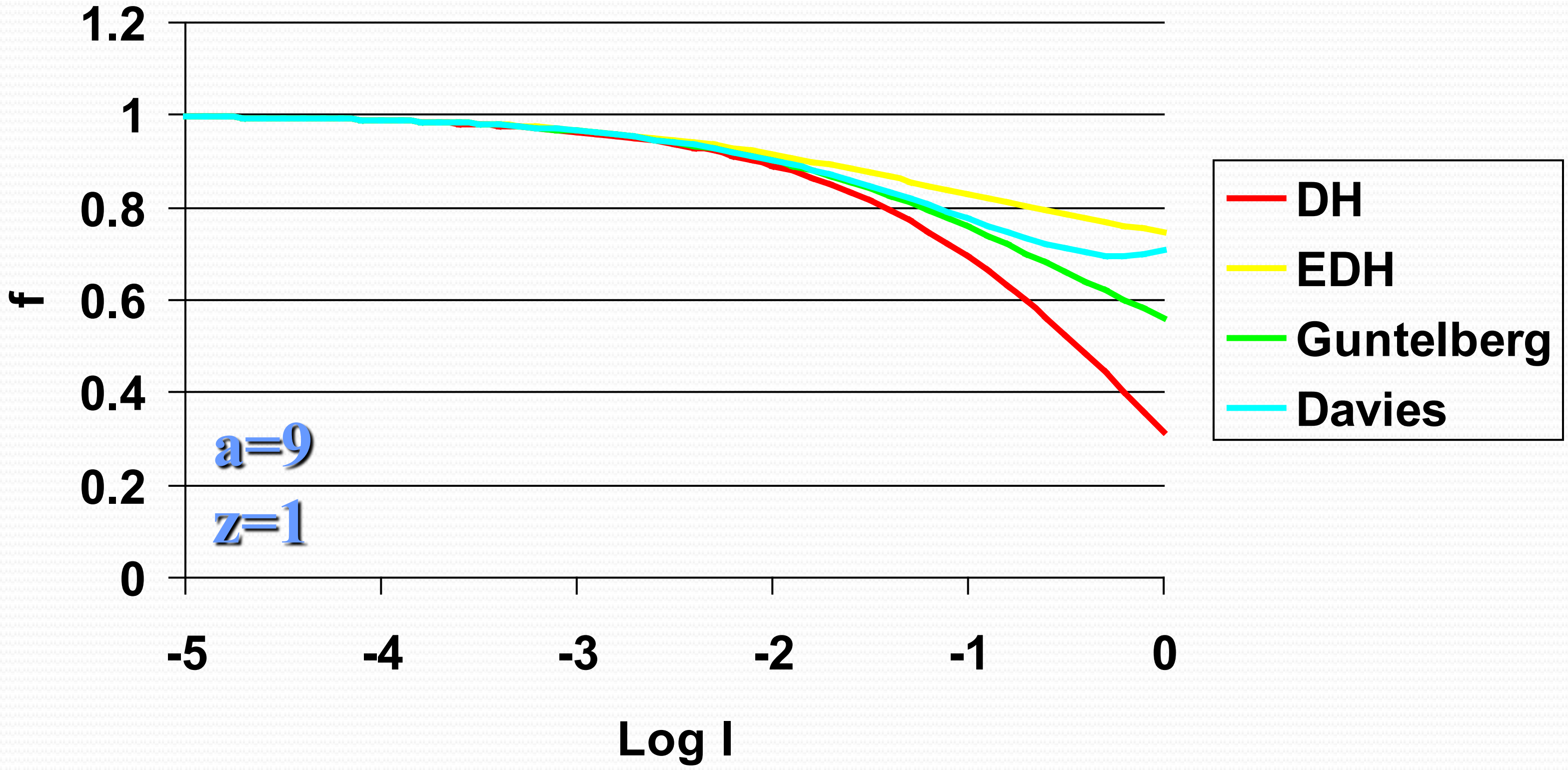
Activity Coefficients compared

- Different approximations at low charge
  - a=3



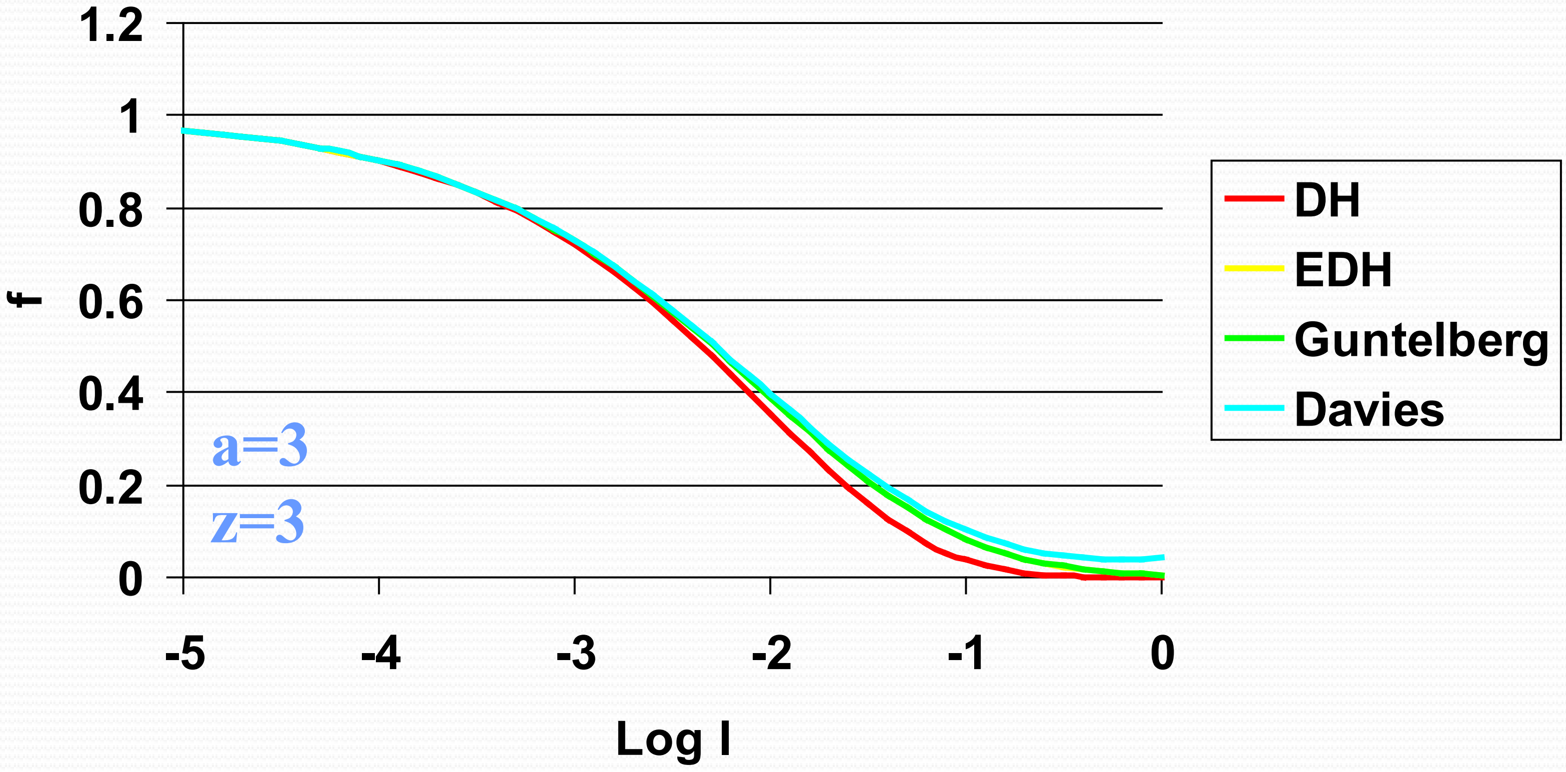
Act. Coeff. Comparison (cont.)

- Different Approximations at low charge
  - a = 9



Act. Coeff. Comparison (cont.)

- Different Approximations at high charge



Calcluation

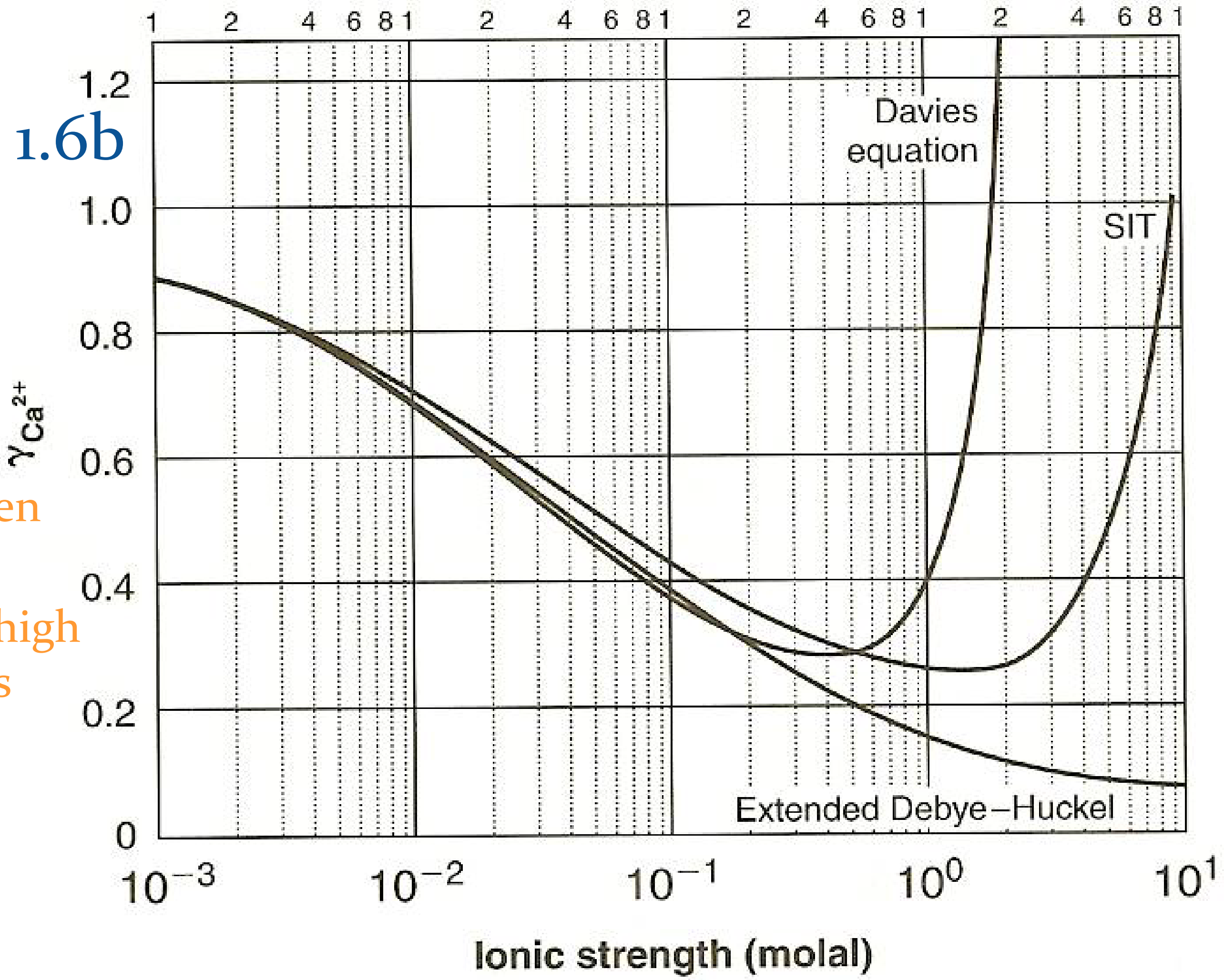
- What is the activity coefficient for ferric iron in a solution of 0.1 M NaCl?
  - Solution
    - Use Extended Debye-Huckel

      $$\log f = -0.5z^2 \frac{\sqrt{I}}{1 + 0.33a\sqrt{I}}$$

    - Determine value of “a” and “I”

Comparison: $CaCl_2$ dissolution

- Benjamin, Figure 1.6b
  - SIT is the specific interaction model
    - Incorporates interactions between specific ions
    - Quite accurate for high brines, but requires more coefficients



Activity Coefficients (cont.)

- For neutral species:
  - $\log\gamma = kI$
    - k is a function of species, T and P
      - $k=0.13$ for O_2 in NaCl
        - in fresh water, $I=0.002$, $\gamma_{O_2} = 1.0006$
- Molar vs. Molal
    - in principle, activity predictions are based on molal concentrations (mole/kg solvent), but since we are often most concerned with dilute solutions, we frequently use molar concentrations

Salting out Coefficients

Compound	*k_s (L/mole)*	*Reference*
Tetrachloroethene	0.213	Gossett, 1987
Trichloroethene	0.186	Gossett, 1987
1,1,1-Trichloroethane	0.193	Gossett, 1987
1,1-Dichloroethane	0.145	Gossett, 1987
Chloroform	0.140	Gossett, 1987
Dichloromethane	0.107	Gossett, 1987
Benzene	0.195	Schwarzenbach et al., 1993
Toluene	0.208	Schwarzenbach et al., 1993
Naphthalene	0.220	Schwarzenbach et al., 1993
Oxygen	0.132	Snoeyink & Jenkins, 1980

Activity for isotopes

- Most subtle of the effects
- For saline waters (chloride is counterion)
  - Deuterium

$$ln\frac{\gamma_{({}^{2}H\,{}^{1}H\,{}^{16}O)}}{\gamma_{({}^{1}H\,{}^{1}H\,{}^{16}O)}} = 0.0022(Na^{+}) + 0.0025(K^{+})$$

$$+0.0051\left(Mg^{+2}\right) + 0.0061\left(Ca^{+2}\right)$$

  - Oxygen-18

$$ln\frac{\gamma_{({}^{1}H\,{}^{1}H\,{}^{18}O)}}{\gamma_{({}^{1}H\,{}^{1}H\,{}^{16}O)}} = 0.0016(K^{+}) - 0.0111\left(Mg^{+2}\right)$$

$$-0.0047\left(Ca^{+2}\right)$$

  - Where () represents the molal concentration (moles/Kg-water)

- To next lecture